

A Simplified Approach for Monitoring Hydrophobic Organic Contaminants Associated with Suspended Sediment: Methodology and Applications

B. J. Mahler, P. C. Van Metre

U.S. Geological Survey, 8027 Exchange Drive, Austin, Texas 78754, USA

Received: 12 March 2002/Accepted: 24 July 2002

Abstract. Hydrophobic organic contaminants, although frequently detected in bed sediment and in aquatic biota, are rarely detected in whole-water samples, complicating determination of their occurrence, load, and source. A better approach for the investigation of hydrophobic organic contaminants is the direct analysis of sediment in suspension, but procedures for doing so are expensive and cumbersome. We describe a simple, inexpensive methodology for the dewatering of sediment and present the results of two case studies. Isolation of a sufficient mass of sediment for analyses of organochlorine compounds and PAHs is obtained by in-line filtration of large volumes of water. The sediment is removed from the filters and analyzed directly by standard laboratory methods. In the first case study, suspended-sediment sampling was used to determine occurrence, loads, and yields of contaminants in urban runoff affecting biota in Town Lake, Austin, TX. The second case study used suspended-sediment sampling to locate a point source of PCBs in the Donna Canal in south Texas, where fish are contaminated with PCBs. The case studies demonstrate that suspended-sediment sampling can be an effective tool for determining the occurrence, load, and source of hydrophobic organic contaminants in transport.

Fish-consumption advisories were in effect for 23% of total lake acreage and 9.3% of total river mileage in the United States in 2000 (US EPA 2001). Many of these advisories were issued for hydrophobic organic contaminants (HOCs), including DDTs, chlordane, and polychlorinated biphenyls (PCBs) (note: in this paper, parent *p,p'*-DDT [1,1'-(2,2,2-trichloroethylidene)bis(4-chlorobenzene)] and its metabolites *p,p'*-DDE and *p,p'*-DDD are referred to collectively as DDTs). Sediment contaminated with HOCs is correlated to adverse effects on the health of benthic organisms and other aquatic biota, and sediment quality guidelines for HOCs and trace elements have been shown to be reliable predictors of toxicity to benthic organisms (MacDonald *et al.* 2000). Not surprisingly, concentrations of HOCs at levels of concern are often found in bottom sediment

of receiving water bodies, particularly in urban areas (Van Metre *et al.* 2000). Yet HOCs are rarely detected in whole (unfiltered) water samples from the urban creeks discharging to contaminated water bodies, even though a major fraction of HOCs is known to be transported in association with suspended sediment (Bradford and Horowitz 1988). As a result, determining loads and sources of HOCs, quantifying the effect of land use on water quality and on the health of aquatic biota, and assessing the efficacy of local recovery programs are problematic.

The chemical quality of suspended sediment is of interest for several reasons. First, suspended sediment is ultimately deposited as bed sediment in a receiving water body, where benthic biota are exposed to it. Second, aquatic biota of all trophic levels, not just bottom dwellers, come into direct contact with sediment in suspension. Third, suspended sediment tends to be more uniform in size and composition than streambed sediment, resulting in less spatial and temporal variability in contaminant concentrations. Fourth, unlike streambed-sediment data, suspended-sediment data, in combination with discharge data, can be used to compute loads and yields of particle-associated contaminants, necessary for making interwatershed comparisons and evaluating the effects of land use on water quality.

The importance of suspended sediment in the transport of HOCs is widely recognized. Some studies have focused on analysis of contaminants associated with suspended sediment for contaminant source determination (Kaiser *et al.* 1985; Zhou *et al.* 2001) or for comparison of concentrations of contaminants associated with suspended sediment to those associated with bed sediment (Long *et al.* 1998). A multidisciplinary study on the Mississippi River analyzed suspended-sediment samples from selected sites along the lower Mississippi River and its major tributaries (Rostad 1997; Rostad *et al.* 1999). Overall, however, the organic chemistry of suspended sediment rarely is measured routinely. For example, the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) program does not include routine suspended-sediment sampling (Gilliom *et al.* 1995), and the USGS National Stream-Accounting Network (NASQAN II) program collects suspended-sediment samples for analysis of major and trace elements at selected sites in large rivers but does not analyze for organic compounds (Hooper *et al.* 1997).

Most monitoring programs collect whole-water (unfiltered) samples for the analysis of HOCs, but HOCs often are not detected in whole-water samples, particularly when suspended-sediment concentrations are less than several hundred mg/L. Benzo(a)pyrene, for example, was not detected in any of 100 storm-event samples from residential sites in the Dallas–Fort Worth area and was detected in less than 5% of samples from commercial and industrial sites (Raines *et al.* 1997). Yet concentrations of benzo(a)pyrene have increased 20-fold in the Dallas–Fort Worth metropolitan area, coincident with urban development, on the basis of an age-dated sediment core from White Rock Lake in Dallas (Van Metre *et al.* 2000); benzo(a)pyrene was detected in semipermeable membrane devices deployed in White Rock Creek (Moring and Rose 1997). The reason that HOCs are rarely detected in whole-water samples, even those that contain highly contaminated suspended sediment, can be explained with a simple illustration. For example, if a sample contains 50 mg/L of suspended sediment, and the sediment contains 17 $\mu\text{g}/\text{kg}$ chlordane (a concentration likely to adversely affect biota health; MacDonald *et al.* 2000), the concentration of chlordane in the whole-water sample will be 0.00085 $\mu\text{g}/\text{L}$. This concentration is orders of magnitude below most laboratory method detection limits—for example, the USGS National Water Quality Laboratory (NWQL) method reporting level for chlordane is 0.1 $\mu\text{g}/\text{L}$.

Analysis of suspended sediment also offers advantages over bed sediment analysis. Although bed sediments are an excellent medium for determination of occurrence of hydrophobic contaminants, they cannot be used to compute contaminant loads and yields. In contrast, suspended-sediment data, in combination with discharge data, can be used to compute particle-associated loads and yields of contaminants, invaluable for making interwatershed comparisons and evaluating the effects of land use on water quality.

Several approaches for the separation of sediment from the water column for chemical analysis have been described (Horowitz 1995; Meade and Stevens 1990; Rees *et al.* 1991), including tangential-flow filtration, decantation, and flow-through centrifugation. Each of these methods has some disadvantages. For example, tangential-flow filtration is labor-intensive and the operating costs are high; decantation requires several days to several weeks. Flow-through centrifugation has become the method of choice for dewatering suspended sediment (Horowitz 1995; Rostad 1997), but purchase and use of the equipment, which is heavy, bulky, and expensive, is impractical for many projects requiring the routine monitoring of suspended-sediment chemistry.

Here we describe a simple methodology for the routine collection of suspended sediment for chemical analysis of organic constituents. The method entails in-line filtration of large volumes of water (from 10 to 1,000 L or more, depending on the suspended-sediment concentration), termed here large-volume suspended-sediment sampling (LVSS). LVSS can be used to obtain sufficient sediment for analysis of organic contaminants, uses equipment that is portable and relatively inexpensive, and can be used either in the laboratory or on site. The method is also applicable for collection and analysis of major and trace elements on suspended sediment. We also present the results of two studies for which LVSS was successfully used, one of which involved investigation of non-point source HOCs, and a second that involved a point source of HOCs.

Materials and Methods

One of the major difficulties in suspended-sediment sampling is obtaining the mass of sediment required to achieve reasonable analytical reporting levels. The sample processing methodology presented here is designed to obtain sufficient sediment for analysis of HOCs, including organochlorine pesticides, PCBs, and polyaromatic hydrocarbons (PAHs). All samples described here were analyzed by the NWQL. Determining concentrations of individual PAHs and most organochlorine compounds by the NWQL at reporting levels ranging from 1 to 10 $\mu\text{g}/\text{kg}$ requires 2–5 g of dry sediment, depending on the degree of contamination of the sediment. Smaller masses of sediment result in proportionally larger reporting levels. Analytical interferences, for example from coextracted high-molecular-weight humic substances, can also raise reporting levels.

The approach used to obtain sufficient sediment for analysis is to separate the sediment from the water column by in-line filtration. If suspended-sediment concentrations exceed about 100 mg/L, a sufficient volume of sample can be collected in 9-L polyethylene carboys loaded into an automated sampler. For suspended-sediment concentrations in the range of 20–100 mg/L, a larger-volume sample can be collected in a commercially available 200-L plastic drum with a removable polytetrafluoroethylene (PTFE) liner. For extremely low suspended-sediment concentrations (< 20 mg/L), if a point sample is adequate and streamflow is not changing rapidly, the filtration can be carried out on site. This approach will have the effect of integrating short-term variations in sediment chemistry over the sampling period. If desired, sand-size and larger particles can be trapped with a 0.63-mm polyester mesh before sample processing.

To obtain the 2–5 g of sediment necessary for analysis of organochlorine compounds and PAHs, water is pumped through either a 298-mm diameter, 0.7- μm pore-size glass-fiber filter (GFF) or a 298-mm diameter, 0.5- μm pore-size PTFE filter using a peristaltic pump. The filter is held in a stainless steel plate filter holder. In the case of the GFFs, the filters are precleaned by baking and are wrapped in aluminum foil pending use. Water is pumped through the GFF until it clogs, then air is pumped through the filter to remove as much water as possible, which improves laboratory minimum reporting levels by decreasing analytical interference. The volume of water pumped is recorded, and samples of whole water for analysis of suspended-sediment concentration (SSC) are collected before and after sample processing. Experience indicates that from about 0.5–2 g of sediment is trapped on each GFF. The filters are placed together in a baked glass jar and chilled for shipment to the laboratory, where the sediment and the GFFs are extracted together. The concentration is reported as mass of organic contaminant per L of water filtered and is converted to mass of organic contaminant per mass of sediment filtered on the basis of the SSC of the original sample.

As an alternative to the GFF, a PTFE filter can be used. The PTFE filter must be sprayed with methanol before placing it on the filter holder to allow water to pass through the filter. Water is pumped through the filter until the filter clogs. The filter then is placed in a locking plastic bag, and a few milliliters of ultrapure or sample water is added. The filter is gently massaged until all the sediment has been removed and is in a slurry in the bottom of the bag. The filter can then be reused for filtration of additional sediment from the same sample, or a new filter can be used. The sediment slurry in the bottom of the bag is placed in a baked glass vial and chilled for shipment to the laboratory. Although more expensive, the PTFE filters have two advantages over the GFFs. First, only the suspended solids are extracted, eliminating the possible interference caused by extraction of the GFF. Second, the concentration is reported as mass of organic contaminant per mass of sediment filtered, eliminating the additional step and resulting uncertainty of converting from mass per volume to mass per mass. The volume of water filtered is measured so that concentration on a mass per volume basis can also be computed. This method is

similar to that employed by Kimball *et al.* (1995) for the analysis of trace elements in suspended sediment.

Organochlorine pesticides, PCBs, PAHs, and alkyl-substituted PAHs (alkyl-PAHs) were extracted, isolated, and analyzed using a variation of the procedures of Foreman *et al.* (1995) and Furlong *et al.* (1996). Briefly, wet sediment was extracted overnight with dichloromethane in a Soxhlet apparatus (note: mention of brand names here and elsewhere in the text is for identification purposes only and does not constitute endorsement by the USGS). The extract was reduced in volume in a Kuderna-Danish concentrator followed by nitrogen gas evaporation and filtered through a 0.2- μm pore size, 25-mm-diameter disposable PTFE membrane syringe filter. Two aliquots of the sample extract were quantitatively injected into a polystyrene-divinylbenzene gel permeation chromatographic (GPC) column and eluted with dichloromethane to remove sulfur and partially isolate the target analytes from coextracted interferences. The first aliquot was analyzed for PAHs and alkyl-PAHs by capillary-column gas chromatography (GC) with detection by mass spectrometry. Variations on the procedures of Furlong *et al.* (1996) for the determination of PAHs include the addition of a silica column cleanup step following the GPC step and the use of selected ion monitoring mass spectrometry to reduce chemical interferences and improve detection limits. The second aliquot was further separated into two fractions by combined alumina/silica adsorption chromatography prior to determination of the organochlorine pesticides and PCBs by dual capillary-column GC with electron capture detection (GC-ECD). Variations on the procedures of Foreman *et al.* (1995) for the determination of organochlorine pesticides and PCBs include the addition of a final micro Fluorosil column cleanup step and quantitation following the procedures of Wershaw *et al.* (1987).

Quality Assurance and Quality Control

At the laboratory level, quality assurance and quality control included analysis of blanks, duplicates, internal standards, spiked material, and certified reference material. More than 90% of all quality control analyses were within acceptable limits as established by the NWQL. Concentrations reported by the NWQL for organics analyses are flagged as “estimated” when they are qualitatively identified as present, but the reported concentrations have a greater uncertainty than usual (Table 1). Situations resulting in an estimate flag include concentrations that are below the NWQL established minimum reporting level but still detectable, samples for which surrogate recovery was not within control limits, and samples from sample sets for which recovery from the set spike was not within control limits (Childress *et al.* 1999). Estimated concentrations were included in computations of loads and yields.

To investigate potential differences between the GFF and PTFE filters, selected samples were split and filtered through each type of filter. Concentrations of organochlorine compounds detected on sediment obtained from the PTFE filter tended to be higher, in some cases up to twice as high as those detected on the GFF filter. The difference in PAH concentrations was more striking, with concentrations on sediments from the PTFE filter two to three times higher than those from the GFF filter. The reason for the difference is not clear. In the PTFE filter method, only the sediment-water slurry is extracted. In the GFF filter method, the sediment and filter are extracted, producing an emulsion that may interfere with quantification of analytes (Mary Olson, NWQL, personal communication). Higher concentrations from the PTFE filters suggests that the methanol used to wet the PTFE filter prior to filtration is not solubilizing contaminants, nor is the PTFE filter sorbing contaminants.

Results

Here we present the results of two case studies with different objectives for which LVSS was successfully used. In the first study, LVSS was used to investigate non-point source pollution. Bed sediment in the receiving water body in an urban area was known to be contaminated, but the extent to which incoming urban creeks were currently contributing to the contamination was not known. LVSS was used to quantify the urban creek contribution. In the second study, LVSS was used to locate a pollution point source. Fish in an irrigation canal were contaminated with PCBs, yet no PCBs had been detected in numerous bed-sediment analyses. Synoptic sampling of the canal using LVSS detected PCBs in suspended sediment and identified potential PCB source areas along portions of the banks.

Case Study 1: LVSS and Non-Point Source Pollution

LVSS was used in Austin to evaluate the contribution of sediment-associated HOCs from two urban creeks to two environments where the HOCs might be affecting the health of aquatic biota. The two creeks contribute sediment to Austin's Town Lake, where fish have been contaminated with chlordane (City of Austin 1992) and one of the creeks under some conditions supplies sediment to the habitat of an endangered salamander (the Barton Springs salamander, *Eurycea sosorum*).

Town Lake is a dammed segment of the Colorado River; because of a series of large reservoirs upstream, most of the sediment entering the lake is transported from several local urban creeks that flow into it (Figure 1). Creeks in the Austin area are ephemeral, thus sediment transport occurs almost exclusively during short-duration runoff events (hours to days in length) in response to storms. The two creeks with the largest watersheds entering Town Lake are Shoal Creek and Barton Creek. Eighty-eight percent of the Shoal Creek watershed is urbanized (Dartiguenave 1997). Only 20% of the entire Barton Creek watershed is urbanized, but 68% of the lower part of the watershed (from Town Lake to the Loop 360 bridge) is urbanized (Figure 1) (Ellen Wadsworth, City of Austin, unpublished data). After heavy rainfall, discharge from these creeks can exceed 30 m³/s and suspended-sediment concentrations can exceed 1,000 mg/L. At these times wide plumes of turbidity are visible in Town Lake downstream from the mouths of Shoal and Barton Creeks.

In addition to its effect on Town Lake, suspended sediment quality in Barton Creek might also affect the habitat of the federally listed Barton Springs salamander that lives only in Barton Springs. During high flow the creek overtops the dam, separating it from the main spring orifice, and deposits a layer of sediment from the creek in the areas where the salamander is found. The salamander and its prey may be susceptible to high concentrations of PAHs (US Fish and Wildlife Service 1997).

The USGS, in cooperation with the City of Austin, began using LVSS in 1999 at one site on Shoal Creek and at two sites—one upstream and one downstream of most of the urban development—on Barton Creek (Figure 1). Automatic sam-

Table 1. Concentrations, loads, and yields of hydrophobic organic contaminants in urban creeks, Austin, Texas

Site ^a	Area (km ²)	Date	Filter Type	Peak Flow (m ³ /s)	Sediment Load (kg)	Chlordane			Total DDT			Total PCBs			Total PAHs			
						Conc. (µg/kg)	Load (mg)	Yield (mg/km ²)	Conc. (µg/kg)	Load (mg)	Yield (mg/km ²)	Conc. (µg/kg)	Load (mg)	Yield (mg/km ²)	Conc. (µg/kg)	Load (g)	Yield (g/km ²)	
B71	232	05/26/99	GFF	6.2	15,000	< 120	b	—	< 37	—	—	< 370	—	—	—	730	4.5	0.046
		05/01/00	GFF	1.2	500	< 63	—	—	< 130	—	—	< 190	—	—	—	820	0.41	0.0018
		06/09/00	GFF	10.2	190,000	< 5.5	—	—	< 1.5	—	—	< 16	—	—	—	96	18	0.078
BAb	311	11/03/00	PTFE	3.1	41,000	< 25	—	—	E ^c 12	490	2.10	< 75	—	—	—	510	21	0.17
		05/06/01	PTFE	8.2	54,000	< 20	—	—	E2.2	120	0.51	< 60	—	—	—	720	38	0.090
		05/18/99	GFF	5.9	10,000	E17	180	0.580	16	170	0.54	< 57	—	—	—	8,000	84	0.27
		05/26/99	GFF	1.2	2,200	48	110	0.34	25	56	0.18	< 130	—	—	—	21,000	48	0.15
		05/02/00	GFF	2.2	500	E39	20	0.063	E7.1	3.6	0.011	< 200	—	—	—	23,000	11	0.037
		06/09/00	GFF	29.7	70,000	< 11	—	—	< 52	—	—	< 34	—	—	—	5,300	370	1.2
SH	33	11/03/00	PTFE	12.5	10,000	< 180	—	—	E22	220	0.71	< 520	—	—	—	16,000	160	0.51
		05/06/01	PTFE	9.9	8,400	< 100	—	—	21	180	0.57	< 300	—	—	—	34,000	290	0.93
		03/18/99	GFF	33.4	360,000	E8.4	3,100	91	13	4,800	144	< 28	—	—	—	21,000	7,700	2.30
		04/26/99	GFF	5.1	20,300	11	220	6.5	13	260	7.7	< 11	—	—	—	15,000	310	9.2
		10/18/99	GFF	1.4	230	250	58	1.7	300	68	2.0	E170	39	1.2	—	57,000	13	0.39
		10/30/99	GFF	9.9	94,000	< 8.7	—	—	5.4	510	15	< 13	—	—	—	9,800	920	28
TLC	—	01/07/00	GFF	22.4	230,000	22	5,000	150	22	5,100	150	53	12,000	360	15,000	3,400	100	
		03/17/00	PTFE	6.2	15,000	56	820	25	E30	440	13	E23	340	10	19,000	280	8.4	
		10/15/00	PTFE	26.3	390,000	53	2,100	610	54	21,000	620	E21	8,100	240	37,000	14,400	430	
		08/26/98	—	—	—	—	—	—	42	—	—	31	—	—	11,400	—	—	
TEC	—	—	—	—	—	—	—	5.3	—	—	—	—	—	60	—	—		
PEC	—	—	—	—	—	—	—	570	—	—	680	—	—	22,800	—	—		

^a B71, Barton Creek at State Highway 71; BAb, Barton Creek above Barton Springs; SH, Shoal Creek at 12th Street; TLC, Town Lake core; TEC, threshold effects concentration [14]; PEC, probable effects concentration [14].

^b —, not computed or not applicable.

^cE, estimated.

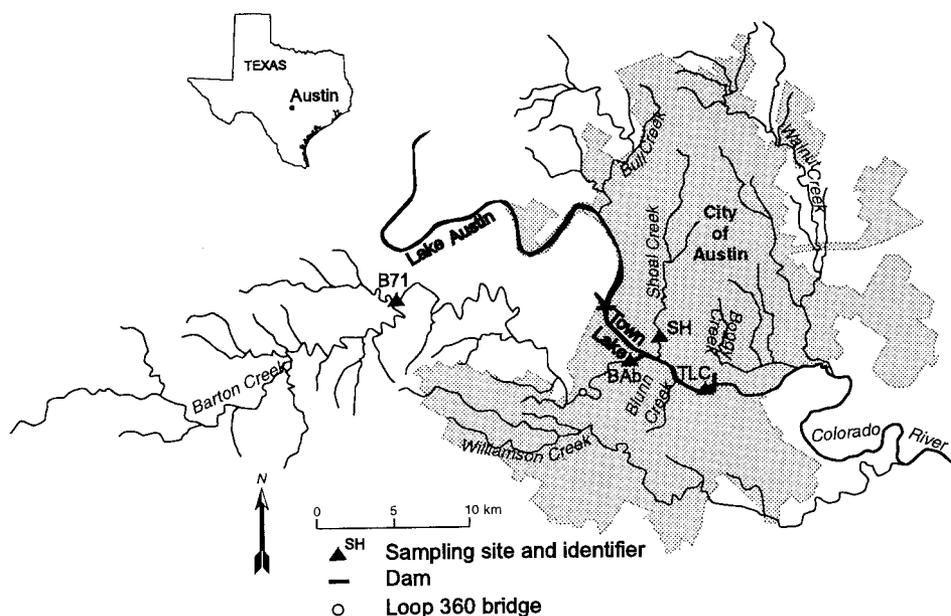


Fig. 1. Locations of sampling sites. B71, Barton Creek at State Highway 71; BAb, Barton Creek above Barton Springs; SH, Shoal Creek at 12th Street; TLC, Town Lake sediment core

plers programmed to collect seven 9-L samples at specified intervals over the storm hydrograph were installed at the three sites. The seven samples were combined to make a flow-weighted composite sample for each event, from which the suspended sediment was separated for analysis and determination of the event mean concentration. The sediment-associated load of a given contaminant was computed as the product of the cumulative stormwater volume associated with the event, the event mean suspended-sediment concentration, and the event mean concentration of the contaminant. The event yield for each contaminant was computed as the event load of the contaminant divided by watershed area.

Contaminant concentrations, loads, and yields for the individual storm events sampled in 1999–2001 are shown in Table 1, as well as the watershed area upstream of each of the sampling sites, the dates of the events sampled, the total sediment load for each event, the peak flow for the event, and, for comparison, contaminant concentrations in the 5-cm interval at the top of a sediment core taken from Town Lake by Van Metre and Mahler (1999). Also shown are the consensus-based sediment quality guidelines (SQGs) compiled by MacDonald *et al.* (2000). The SQGs have been shown to be a reliable predictor of sediment toxicity to benthic biota. Because the SQGs are based on toxicity of bed sediments, they do not directly apply to the toxicity of whole water containing contaminated suspended sediments. However, the SQGs can be compared to sediment-associated contaminant concentrations to evaluate relative suspended sediment quality at different sites, particularly given that suspended sediments ultimately do settle out of flow to become bed sediments in a receiving water body.

Sorption characteristics of the suspended sediment samples from the different sites, on the basis of organic carbon concentrations and grain size, were similar and showed little within-site variation. Average concentrations of organic carbon at the three sites were 3.0, 3.7, and 2.2 mg/L for upstream Barton Creek, downstream Barton Creek, and Shoal Creek, respectively, with standard deviations of 0.8 or less. The overall

particle-size distributions at the sites were also similar, based on the silt/sand separation: the weight percent of particles greater than 0.063 mm in diameter was in all cases less than 5%, with averages of 1.5, 1.8, and 2.0 for upstream Barton Creek, downstream Barton Creek, and Shoal Creek, respectively, and standard deviations of 1.4 or less. The similar organic carbon concentrations and particle-size distributions suggests that significant differences in particle-associated concentrations, loads, and yields can be attributed to differences in anthropogenic sources and not gross differences in sediment properties. Furthermore, the average suspended-sediment particle size tended to be much smaller than that of bed-sediment samples, and the grain-size distribution showed much less variability. For example, the average percentage of particles in bed sediments from the downstream Barton Creek site with a diameter greater than 0.063 mm was 67, with a standard deviation of 36 (Leila Gosselink, City of Austin, unpublished data).

Suspended sediment concentrations were greater at Shoal Creek than at either of the Barton Creek sites, with medians of 480, 110, and 900 mg/L for upstream and downstream Barton Creek and Shoal Creek, respectively. Concentrations of some major elements in suspended sediments differed between sites as well, with higher aluminum and lower calcium concentrations at Shoal Creek than at Barton Creek. The Barton Creek watershed is mostly underlain by limestone and dolomite, and Shoal Creek is underlain by areas of chalk, clay, and alluvial deposits (Garner and Young 1976). These differences and the greater degree of urbanization could explain the greater SSC and major element differences in Shoal Creek relative to Barton Creek. Field observations of turbid runoff from active construction sites could explain the surprisingly high SSC at the upstream Barton Creek site. One possible effect of the differences in SSC among sites is that contaminant concentrations could be affected by variable amounts of dilution from “clean” soils. Conversion of concentrations to contaminant loads and yields factors out this dilution effect.

The contribution to the total load from dissolved and colloid-associated transport was not measured. Its relative importance is a function of whether or not the water and suspended sediment are in equilibrium, the solubility of the contaminant, the colloid-sized particle concentration, the dissolved organic carbon concentration, and the suspended sediment concentration. Knowing the concentration on the particle-associated phase, if equilibrium is assumed, the concentration of organic contaminants in the dissolved phase can be estimated based on published partition coefficients. If colloidal concentrations are ignored, the total load can be computed as the sum of the load in the dissolved phase and the particle-associated phase. The particle-associated loads computed here are estimated to represent medians of 35% of the total load of organochlorine compounds, 11% of the total load of the two- and three-ring PAHs, and 41% of the total load of the four- to six-ring PAHs. Although it is unlikely that these systems are at chemical equilibrium, and that therefore the particle-associated load probably represents a greater percentage of the total load than that computed, the total loads almost certainly exceed the particle-associated loads reported here.

In general, HOC occurrence and particle-associated load and yield increased with increasing urbanization of the contributing watershed (Table 1; Figure 2). At the upstream Barton Creek site, chlordane and PCBs were not detected; DDT, when detected, was at the lower end of concentrations detected at the other two sites. Total PAH concentrations, with a median of 730 $\mu\text{g}/\text{kg}$, were approximately 25 times less than concentrations at the more urbanized sites. At the downstream Barton Creek site, the next most urbanized site, PCBs were not detected, but chlordane was detected in one-half of the samples, and one or more of the DDTs were detected in five of six samples. The median total-PAH concentration of 18 500 $\mu\text{g}/\text{kg}$ was similar to the median of 19,000 $\mu\text{g}/\text{kg}$ at Shoal Creek, the most urbanized site. The similarity to Shoal Creek and the large increase compared to the upstream site indicates that urbanization in the watershed is having a significant impact on sediment quality at the downstream Barton Creek site. Of seven samples collected at Shoal Creek, PCBs were detected in four, chlordane in six, and DDTs in all.

Although loads and yields could not be determined on an annual basis, it is evident from the event data that the loads of chlordane, DDTs, and PAHs transported to Town Lake by Shoal Creek greatly exceed those transported by Barton Creek, and that differences in yields indicate that the Shoal Creek watershed produces far greater amounts of these HOCs per watershed area than the Barton Creek watershed. Median yields of total DDT and total PAHs, for example, are approximately 30 and 70 times greater at Shoal Creek than at the downstream Barton Creek site. The much greater load of all contaminants contributed to Town Lake by Shoal Creek is a result of the higher suspended-sediment concentrations combined with the large number of organochlorine compound detections and relatively high contaminant concentrations. Concentrations of contaminants associated with suspended sediment at Shoal Creek and Barton Creek were similar, yet because the areal extent of the Shoal Creek watershed is almost 10 times smaller than that of Barton Creek, the contaminant yields from Shoal Creek exceed those of Barton Creek by one to three orders of magnitude, demonstrating a link between land use and contaminant yield. Though bed-sediment sam-

pling might have demonstrated the similarity in contaminant concentrations at the two sites, use of the suspended-sediment sampling approach allows the land-use impact analysis to be carried one step further.

Concentrations of HOCs analyzed in the incoming suspended sediment are similar to concentrations of HOCs at the top of the core from Town Lake, the receiving water body (Figure 2). Concentrations of chlordane, DDT, PCBs, and PAHs detected in the top 5 cm of the sediment core from the lake are bracketed by those detected in suspended sediment from both Shoal and Barton Creeks. SQGs, developed to predict toxicity of bed sediments to benthic biota, can be used to evaluate the potential toxicity of lake sediments. The similarity between concentrations of contaminants in bed sediment from the receiving water body and those of suspended sediment being transported to that water body supports the use of SQGs as a screening tool for evaluating the ultimate toxicity of suspended sediment at the creek sites.

The use of LVSS in Austin provided information that could not have been obtained by use of conventional methods of whole-water or bed-sediment sampling and analysis. HOCs on occasion have been detected in samples of whole water from Shoal Creek but at frequencies and concentrations that preclude computation of loads (Gandara *et al.* 1996). Elevated concentrations of HOCs have been detected on bed sediment from Shoal Creek (Leila Gosselink, City of Austin, unpublished data), but these data cannot be converted to loads or yields. In contrast, chlordane and DDT were detected in every suspended-sediment sample analyzed from Shoal Creek, allowing quantification of particle-associated loads. The results from this study indicate that if HOCs are present in the water column, the likelihood of detecting them and the usefulness of the resulting data are both increased by using LVSS rather than whole-water or bed-sediment sampling.

Case Study 2: LVSS and Point-Source Pollution

The search for the source of PCBs in the Donna Canal in south Texas illustrates the usefulness of LVSS as a tool for locating point sources of HOCs. Fish in the canal have elevated concentrations of PCBs in their tissue, yet prior to the use of LVSS, PCBs had not been detected in the canal using the more traditional approach of bed-sediment sampling.

The Donna Canal conveys water for irrigation and drinking-water supply from the Rio Grande to Donna Reservoir near Donna (Figure 3). In 1993, a fillet from a carp caught in the canal had a PCB concentration of 399,000 $\mu\text{g}/\text{kg}$ (US EPA 1994). As a result of this extremely high concentration—the US EPA national criterion for edible fish tissue is 14 $\mu\text{g}/\text{kg}$ —additional fish were collected for analysis. Since 1993, PCBs have been detected in 18 of the 31 fish collected from the Donna Canal, at concentrations as high as 24,000 $\mu\text{g}/\text{kg}$. A fish-possession ban for the canal was issued in 1993, but subsistence fishing is prevalent in this part of Texas, and the Donna Canal remains a popular fishing location despite the ban.

From 1993 to 1997, 31 samples of bed sediment from the canal were analyzed by various agencies, but no PCBs were detected (Buchanan 1997). Much of the canal is cement-lined,

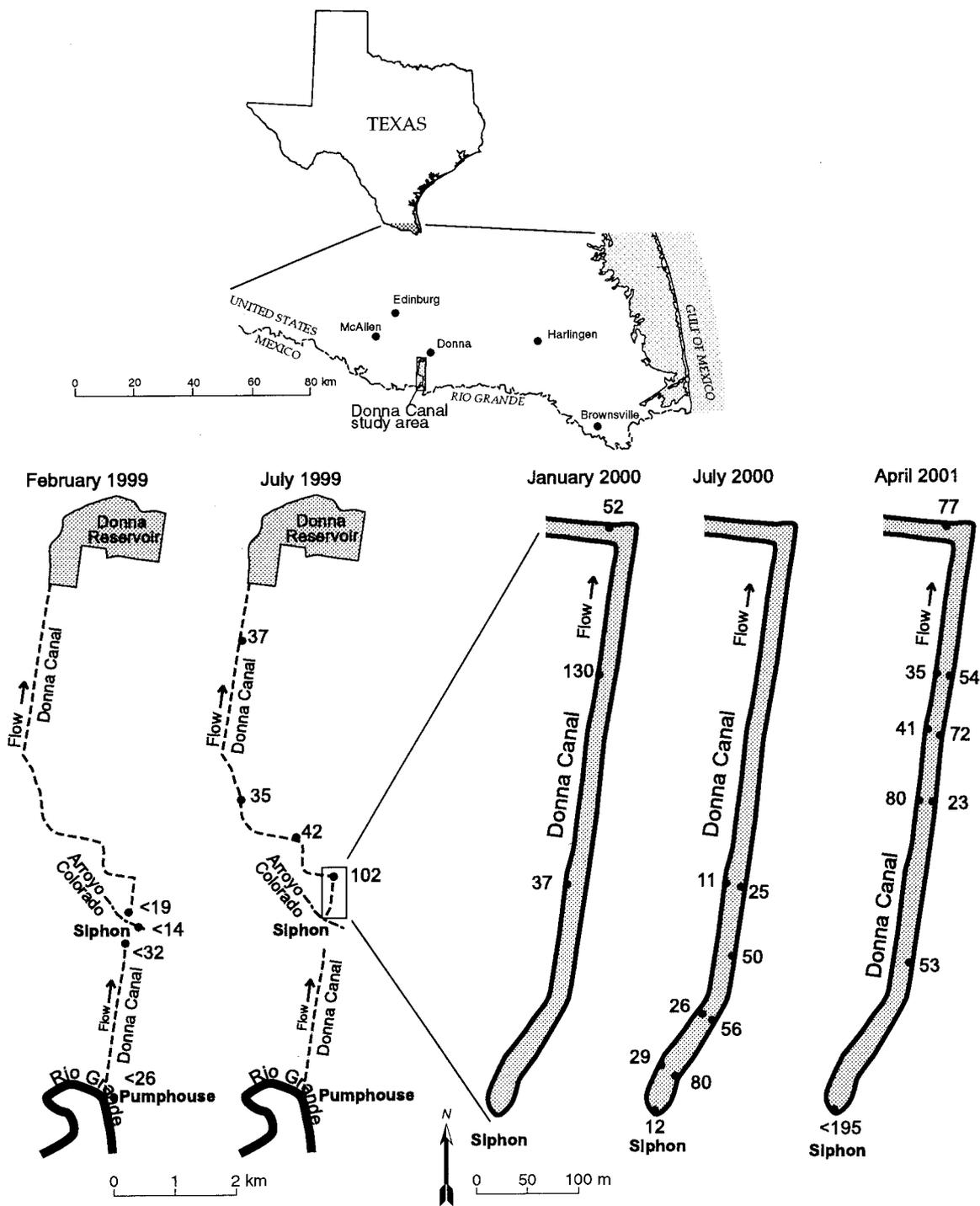


Fig. 3. Location of study site and locations of sampling sites and concentrations (µg/kg) of PCBs detected on suspended sediment in the Donna Canal

use this information to determine how best to remediate contamination of the Donna Canal.

Why is suspended-sediment sampling a better approach for point-source determination than collection of water or bed-sediment samples? The case against sampling whole water for HOCs has already been described—even highly contaminated sediment can be diluted to a concentration below detection

limits for whole-water samples. The advantage of LVSS over bed-sediment sampling is less intuitive. We hypothesize that for a point source, bed-sediment sampling at discrete intervals is likely to miss the source, unless the point source is very broad or the sampling intervals are extremely narrow. In contrast, suspended sediment tends to integrate the contaminant, diffusing it along the transport pathway downstream from the

source. Although the contaminated sediment, once suspended, becomes increasingly diluted by uncontaminated sediment with distance from the point source, it remains detectable by LVSS at distances of more than a kilometer from the source. Additionally, in most streams, the sorting action of suspension and transport results in a finer grain size and higher organic carbon concentration in suspended sediment than bed sediment, usually correlated with higher concentrations of HOCs.

It is surprising that relatively low concentrations of PCBs in the environment have resulted in such high concentrations in the fish at the Donna Canal. The concentrations of PCBs detected on suspended sediment in the Donna Canal are not remarkably high compared to concentrations in bed sediment from other lakes with fish-consumption advisories for PCBs, and concentrations on the bed sediment sampled have all been below the detection limit of 20 $\mu\text{g}/\text{kg}$ per Aroclor, yet the average PCB concentration for fish sampled from the canal is 3,000 $\mu\text{g}/\text{kg}$ (Buchanan 1997). This contrasts markedly to many other water bodies under fishing advisories for PCBs, in which the PCB concentrations in the bed sediment and in the fish are similar. For example, in Mountain Creek Lake (near Dallas), a fishing advisory was issued because the fish contained an average concentration of 330 $\mu\text{g}/\text{kg}$ of PCBs, and PCB concentrations in surficial sediment from the contaminated part of the lake averaged 292 $\mu\text{g}/\text{kg}$ (Lisa Williams, Texas Department of Health, personal communication; Jones *et al.* 1997). Why is bioaccumulation of PCBs so high in the Donna Canal? One possibility is that because sediment in the canal is kept in suspension by the flow in the canal, the exposure pathway to fish is more direct. Contaminants associated with suspended sediment have been shown to be more bioavailable than those associated with bed sediment (Menon and Menon 1999). In the Donna Canal, higher-trophic-level fish, such as bass, as well as bottom feeders such as carp and catfish, were contaminated with PCBs (Buchanan 1997). In contrast, at Mountain Creek Lake the higher-trophic-level fish were not as contaminated and no evidence of biomagnification was seen, even though contamination of higher-trophic-level fish is assumed to occur through predation (Jones *et al.* 1997). This raises the possibility that overall, contaminated sediment in suspension might pose a more direct threat to the health of fish than contaminated bed sediment.

Conclusions

Information on HOCs in aquatic systems, including occurrence, loads, and sources, often can be better obtained through the collection and analysis of suspended sediment rather than whole-water or bed-sediment samples. This was illustrated here by examining the detection limitations of whole-water sample analysis versus analysis of suspended sediment and by two case studies. HOCs associated with suspended sediment might escape detection in whole-water samples but can be quantified by separating the solids and analyzing them directly. Use of filters of the appropriate size and material and filtration of large volumes of water allow efficient removal of sufficient sediment for laboratory analysis of organic contaminants. The results can be combined with discharge data for the computation of contaminant loads and yields.

A case study in Austin demonstrated that the occurrence of HOCs on suspended sediment in urban creeks was related to urban land use and was consistent with the occurrence of HOCs in sediment from the receiving water body. Flow-weighted composite samples of suspended sediment collected over the storm hydrograph allowed computation of particle-associated event loads and yields of contaminants. From the results, it was clear that the more urbanized of two creeks was contributing the majority of the load of several different HOCs to the receiving water body, despite similar contaminant concentrations in and the greater watershed area of the other creek. These results could not have been obtained either from whole-water sampling, which would have produced mostly nondetections, or from bed-sediment sampling, from which loads and yields could not have been computed.

A case study of the Donna Canal in south Texas illustrated the utility of LVSS for determining the source of HOCs. LVSS successfully detected PCBs in an area where analysis of numerous water and bed-sediment samples had produced nondetections. Using LVSS, the probable source of PCBs to the Donna Canal was narrowed down to a 600-m-long reach of the canal.

References

- Bradford WL, Horowitz AJ (1988) The role of sediments in the chemistry of aquatic systems. Proceedings of the Sediment Chemistry Workshop, February 8–12, 1982, Reston, VA, US Geological Survey Circular 969, 75 pp
- Buchanan TA (1997) Polychlorinated biphenyls in fish in the Donna Reservoir and canal system and in the lower Rio Grande Valley of Texas. Masters thesis, School of Public Health, University of Texas Health Science Center at Houston, Houston, TX
- Childress CJO, Foreman WT, Connor BF, Maloney TJ (1999) New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U.S. Geological Survey National Water Quality Laboratory. US Geological Survey Open-File Report 99–193, 19 pp
- City of Austin (1992) Diagnostic Study of Water Quality Conditions in Town Lake, Austin, Texas. Vol I, 378 pp
- Dartiguenave CM (1997) Water quality master planning for Austin. Masters thesis, University of Texas, Austin, TX
- Foreman WT, Connor BF, Furlong ET, Vaught DG, Merten LM (1995) Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of organochlorine pesticides and polychlorinated biphenyls in bottom sediment by dual capillary-column gas chromatography with electron-capture detection. US Geological Survey Open File Report OFR 95–140, 78 pp
- Furlong ET, Vaught DG, Merten LM, Foreman WT, Gates PM (1996) Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of semivolatile organic compounds in bottom sediment by solvent extraction, gel permeation chromatographic fractionation, and capillary-column chromatography/mass spectrometry. US Geological Survey Open File Report OFR 95–719, 67 pp
- Gandara SC, Gibbons WJ, Andrews FL, Jones RE, Barbie DL (1996) Water resources data Texas water year 1996. US Geological Survey Water-Data Report TX-96–3:100–102
- Garner LE, Young KP (1976) Environmental geology of the Austin area: an aid to urban planning. Bureau of Economic Geology, University of Texas at Austin, Report of Investigations no. 86
- Gilliom RJ, Alley WM, Gurtz ME (1995) Design of the National

- Water-Quality Assessment Program; Occurrence and Distribution of Water-Quality Conditions. US Geological Survey Circular 1112, 33 pp
- Hooper RP, Goolsby DA, Rickert DA, McKenzie SW (1997) NASQAN—a program to monitor the water quality of the nation's large rivers. US Geological Survey Fact Sheet FS-055-97, 6 pp
- Horowitz AJ (1995) The use of suspended sediment and associated trace elements in water quality studies. IAHS Press, Wallingford, Oxfordshire, IAHS Special Publication no. 4
- Jones SA, Van Metre PC, Moring JB, Braun CL, Wilson JT, Mahler BJ (1997) Chemical data for bottom sediment, lake water, bottom-sediment pore water, and fish in Mountain Creek Lake, Dallas, Texas, 1994–6. US Geological Survey Open-File Report 97–245, 50 pp
- Kaiser KLE, Tkacz RJ, Platford RF, Comba ME, Hunter H, Maguire RJ (1985) Trace organic contaminants in the Detroit River. *J Great Lakes Res* 11:386–399
- Kimball BA, Callender E, Axtmann EV (1995) Effects of colloids on metal transport in a river receiving acid mine drainage, Upper Arkansas River, Colorado, U.S.A. *Appl Geochem* 10:285–306
- Long JLA, Rae JE, House WA, Parker A (1998) Micro-organic compounds associated with sediments in the Humber rivers. *Sci Total Environ* 210-211:229–253
- MacDonald DD, Ingersoll CG, Berger TA (2000) Development and evaluation of consensus-based quality guidelines for freshwater ecosystems. *Arch Environ Contam Toxicol* 39:20–31
- Meade RH, Stevens HHJ (1990) Strategies and equipment for sampling suspended sediment and associated toxic chemicals in large rivers—with emphasis on the Mississippi River. *Sci Total Environ* 97/98:125–135
- Menon NN, Menon NR (1999) Uptake of polycyclic aromatic hydrocarbons from suspended oil borne sediments by the marine bivalve *Sunetta scripta*. *Aquat Toxicol* 45:63–69
- Moring JB, Rose DR (1997) Occurrence and concentrations of polycyclic aromatic hydrocarbons in semipermeable membrane devices and clams in three urban streams of the Dallas–Fort Worth metropolitan area, Texas. *Chemosphere* 34:551–566
- Raines TH, Baldys S III, Lizarraga JL (1997) Characterization of storm water runoff from the Naval Air Station and Naval Weapons Industrial Reserve Plant, Dallas, Texas, 1994–1996. US Geological Survey Open-File Report 97-402, 80 pp
- Rees TF, Leenheer JA, Ranville JF (1991) Use of a single-bowl continuous-flow centrifuge for dewatering suspended sediments: effect on sediment physical and chemical characteristics. *Hydrol Proc* 5:201–214
- Rostad CE (1997) Concentration and transport of chlordane and nonachlor associated with suspended sediment in the Mississippi River, May 1988 to June 1990. *Arch Environ Contam Toxicol* 33:369–377
- Rostad CE, Pereira WE, Leiker TJ (1999) Distribution and transport of selected anthropogenic lipophilic organic compounds associated with Mississippi River suspended sediment, 1989–1990. *Arch Environ Contam Toxicol* 36:248–255
- US EPA (Environmental Protection Agency) (1994) Lower Rio Grande Valley environmental monitoring study: report to the community in the pilot project. US EPA, Washington, DC
- US EPA (2001) Update: national listing of fish and wildlife advisories. EPA-823-F-01-010, 4 pp
- US Fish and Wildlife Service (1997) Final rule to list the Barton Springs salamander as endangered. *Fed Reg* 62:23377–23392
- Van Metre PC, Mahler BJ (1999) Town Lake bottom sediments: a chronicle of water-quality changes in Austin, Texas, 1960–98. US Geological Survey Fact Sheet FS-183-99, 6 pp
- Van Metre PC, Mahler BJ, Furlong ET (2000) Urban sprawl leaves its PAH signature. *Environ Sci Technol* 34:4064–4070
- Wershaw RL, Fishman MJ, Grabbe RR, Lowe LE (1987) Methods for the determination of organic substances in water and fluvial sediments. US Geological Survey Techniques of Water-Resources Investigations, book 5, chap A3, 80 pp
- Zhou JL, Hong HS, Wang ZD, Maskaoui K, Qiu YW (2001) Polychlorinated biphenyl congeners and organochlorine insecticides in the water column and sediments of Daya Bay, China. *Environ Pollut* 113:373–384